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Description

This invention relates to a photopolymerizable composition for cladding optical fibers.

As discussed in, for example, Blyler and Aloisio, Polymer coatings for optical fibers, Chemtech, 5 November 1987, pages 680-684, optical fibers consist of a central core, usually a highly transparent glass (silica, often containing various doping materials) surrounded by a cladding with a refractive index lower than that of the glass; this cladding serves to confine light within the central core in order to reduce radiation losses from the surface of the core, and hence reduce attenuation of radiation travelling along the core.

10 In most optical fibers, the cladding is formed from a second glass. Because minor flaws in such a glass cladding greatly reduce the tensile strength of the optical fiber, it is customary to provide the fiber with a secondary, protective cladding, which is usually formed from a polymeric material. For example, US-A-4 558 082 and US-A-4 663 185 describe acrylated silicone polymers useful as, *inter alia*, optical fiber 15 claddings. These silicone polymers are prepared by reacting limonene oxide-functional silicones with acrylic acid or a substituted acrylic acid in the presence of a catalyst, which can be a tetraalkylurea or a tetraalkylguanidine.

Acrylic resins have also been used as protective claddings for optical fibers. US-A-4 427 823 describes an uncured, filled coating composition comprising 100 parts by weight of (a) a polyfunctional acrylic-type carboxylic acid ester monomer or its prepolymer, this monomer or prepolymer being composed of 0 to 75 percent by weight tri- or higher acrylates, and 25 to 100 percent diacrylate; (b) 0.001 to 20 parts by weight of a polymerization initiator; and (c) 5 to 250 parts by weight of an inorganic solid filler having a refractive index of 1.40 to 1.60 and an average first-order particle diameter of at least 1 μm but less than 1 μ .

According to the aforementioned Blyler and Aloisio article, polymer-clad fibers usually consist of a silica core clad with either a poly(dimethylsiloxane) resin or a fluorinated acrylic polymer. For example, US-A-4 568 566 describes photocurable silicone compositions, useful as optical fiber claddings, which compositions contain chemically combined siloxy units and units of the formula R_2SiO , where a number of the R units are acrylate or alkyl-substituted acrylate ester groupings.

However, silicone primary claddings have a number of serious disadvantages. The viscosity and curing requirements of the silicones restrict the production rate of the clad fiber to about 0.5 meters/sec. Silicone 30 claddings do not adhere well to quartz, and the softness of the cladding leads to difficulties in connecting the clad fiber to other components of the optical system; temperature changes can cause the quartz core to be forced into and out of the cladding at the connection. Furthermore, according to US-A-4 511 209, exposing the silicone-clad optical fibers to low temperatures in the range of -40° to -50°C results in an increase in attenuation of 10-20 dB/km; in many cases an increase in room temperature attenuation occurs 35 after the fiber has been exposed to such low temperatures.

It is also known that fluorine-containing materials can be incorporated into claddings containing acrylates and methacrylates. For example, US-A-4 508 916 describes curable substituted urethane acrylates and methacrylates having an aliphatic backbone with at least one pendant fluorinated organic group attached thereto, this backbone being end-capped with an acrylic or methacrylic group.

40 US-A-5 024 507 describes and claims a photopolymerizable composition capable of being polymerized upon exposure to ultraviolet light, the composition forming upon photocuring a cured composition having a refractive index not greater than about 1.43, and comprising a substantially homogeneous mixture of:
 a) an unsubstituted or fluorosubstituted diacrylate monomer;
 b) a fluorinated monofunctional acrylate monomer in an amount of from about 2 to about 12 parts by 45 weight per part by weight of the diacrylate monomer;
 c) a photoinitiator; and
 d) a viscosity modifying agent in an amount sufficient to increase the viscosity of the composition to a value in the range of from about 1000 to about 15000 cP.

Example 4 of this application shows the production, from a preferred photopolymerizable composition, of a 50 cured polymer having a refractive index of 1.378.

Although the claddings described in this patent are satisfactory for many purposes, there are certain applications, for example, coupling the output of a laser diode to an optical fiber, where a cladding with an even lower refractive index is desirable in order to provide an optic fiber with a higher numerical aperture and coupling efficiency. However, the present inventor has found that if one attempts to produce a very low 55 refractive index cladding using the compositions described in this patent by employing a highly fluorinated diacrylate monomer, a highly fluorinated monoacrylate monomer and, as the viscosity modifying agent a homopolymer of a highly fluorinated monoacrylate, unsatisfactory results are obtained. Firstly, during polymerization of a solution of the viscosity modifying agent in the monomer mixture, substantial haze

develops, apparently because of phase separation between the polymer being produced and the viscosity modifying agent. Secondly, most available photoinitiators are insoluble in the mixture of highly fluorinated acrylate monomers, and even diethoxyacetophenone, which is somewhat soluble in the monomer mixture, becomes incompatible and gives very hazy mixtures in the presence of the viscosity modifying agent.

5 It has now been discovered that the aforementioned problems can be eliminated, or at least substantially reduced, by first reacting a photoinitiator monomer having both a photoinitiating group and an ethylenically unsaturated group with a fluorosubstituted monomer having an ethylenically unsaturated group to form a copolymer having pendant photoinitiating groups, and then using this copolymer as a combined viscosity modifying agent and photoinitiator in a photopolymerizable composition comprising also a fluorosubstituted diacrylate.

10 This invention provides a process for cladding an optical fiber, which process comprises:
coating the optical fiber with a layer of a photopolymerizable composition; and
exposing the coated optical fiber to ultraviolet light, thereby curing the photopolymerizable composition to produce a cladding on the optical fiber,

15 characterized in that the photopolymerizable composition is a photopolymerizable composition of the present invention.

Accordingly, this invention provides a photopolymerizable composition capable of being polymerized upon exposure to ultraviolet light and comprising a fluorosubstituted diacrylate, the composition being characterized in that it also comprises a copolymer of the present invention, said copolymer having repeating units from a fluorosubstituted monomer having an ethylenically unsaturated group. This copolymer is characterized in that it also has repeating units from a photoinitiator monomer having both a photoinitiating group and an ethylenically unsaturated group, these repeating units from the photoinitiator monomer providing pendant photoinitiating groups in the copolymer.

20 This invention also provides a process for the preparation of such a copolymer; this process is characterized by reacting a photoinitiator monomer having both a photoinitiating group and an ethylenically unsaturated group with a fluorosubstituted monomer having an ethylenically unsaturated group.

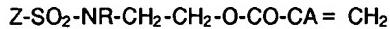
25 The accompanying drawing shows schematically an apparatus which can be used to carry out the process of the invention for cladding an optic fiber.

30 As already mentioned, in the process of the present invention a photoinitiator monomer having both a photoinitiating group and an ethylenically unsaturated group is reacted with a fluorosubstituted monomer having an ethylenically unsaturated group to produce a copolymer having pendant photoinitiating groups. This copolymer is then mixed with a fluorosubstituted diacrylate to form a photopolymerizable composition, which can be coated onto an optical fiber and cured by exposure to ultraviolet light, thereby forming a cladding on the fiber.

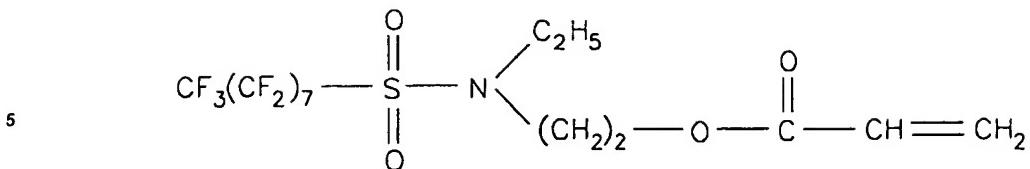
35 The fluorosubstituted monomer used to form the copolymer of the present invention is preferably a monoacrylate or mono-methacrylate, the monoacrylates generally being preferred over the methacrylates because of their lower refractive indices. Desirably, the monoacrylate is one in which a minimum of three C-F bonds exist and in which at least 25 percent of the C-H bonds in the corresponding unsubstituted monomer have been replaced with C-F bonds. Desirably, the monomer will contain from 30 to 65 percent 40 by weight of fluorine. Among the monoacrylates which may be used are, for example, those of the formula:



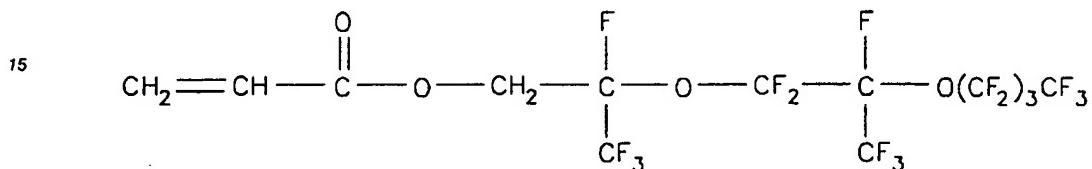
45 where Y is a perfluoroalkylene grouping and T is fluorine or a -CF₂H group. The fluorinated monoacrylate may also contain heteroatoms such as sulfur, oxygen and nitrogen; examples of such monomers are those of the formula:



50 where Z is H(CF₂)_m or F(CF₂)_m, where m is an integer from 3 to 12, R is an alkyl group and A is hydrogen or methyl. Examples of commercially available monoacrylates which may be useful in the present process are 1H,1H,5H-octafluoropentyl acrylate, trifluoroethyl acrylate and heptafluorobutyl acrylate, all of which are available from PCR Incorporated, P.O. Box 1466, Gainesville, Florida 32602, United States of America, and



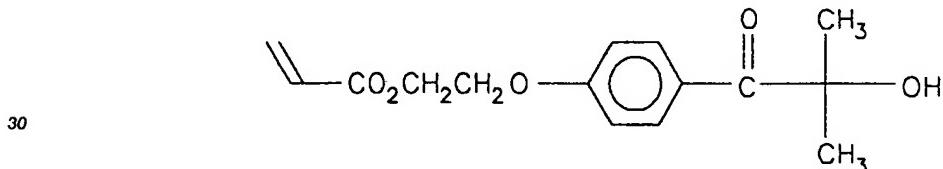
which is available from Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, United States
10 of America under the tradename FX-13. Desirably, the fluorosubstituted monoacrylate comprises a fluorosubstituted polyether, an especially preferred polyether being that of the formula:



20 which is available from Minnesota Mining and Manufacturing Company under the tradename L-9911.

The ethylenically unsaturated group of the photoinitiator monomer used in the present invention is preferably an acrylate or methacrylate group. Preferred (meth)acrylates are (meth)acrylates of a phenoxyal-kanol or a phenylalkanol; a specific preferred photoinitiator is that of the formula:

25



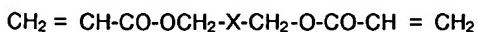
which is sold by EM Industries, Inc, 5 Skyline Drive, Hawthorne, NY 10532, United States of America, under
35 the tradename Darocur ZLI-3331.

The copolymerization of the photoinitiator monomer and the fluorinated monomer should of course be carried out so that only the ethylenically unsaturated groups of the two monomers react, and essentially no reaction of the photoinitiator groups of the photoinitiator monomer occurs. Catalysts capable of causing the reaction of ethylenically unsaturated groups without causing reaction of photoinitiator groups are of course well-known to those skilled in the polymer art, and are commercially available. One specific catalyst which has been found to give good results in the present process is azobis(isobutyronitrile) (AIBN). The mixture of the photoinitiator monomer and the fluorinated monomer, and the resultant copolymer, should of course be screened from radiation (typically ultraviolet radiation) liable to cause reaction of the photoinitiator groups until the photopolymerizable composition has been applied to the optical fiber.

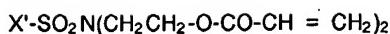
45 The optimum molar ratio of photoinitiator monomer to fluorinated monomer may readily be determined empirically; this molar ratio affects the degree of cross-linking in the final cladding, and hence the physical properties of that cladding. Typically, from about 0.02 to about 0.2 moles of photoinitiator monomer will be used per mole of fluorinated monomer. The copolymerization of the photoinitiator monomer and the fluorinated monomer is conveniently effected in a fluorinated solvent; both ethyl trifluoroacetate and 1,3-bis-(trifluoromethyl)benzene (hexafluoro-m-xylene, or HFX) may be used as solvents, although the latter is preferred since the former may be toxic due to its ready hydrolysis to trifluoroacetic acid.

50 The fluorosubstituted diacrylate used in the present process desirably contains at least about 25 percent, and preferably from about 25 to about 65 percent by weight fluorine. A preferred group of fluorosubstituted diacrylates are those of the formulae:

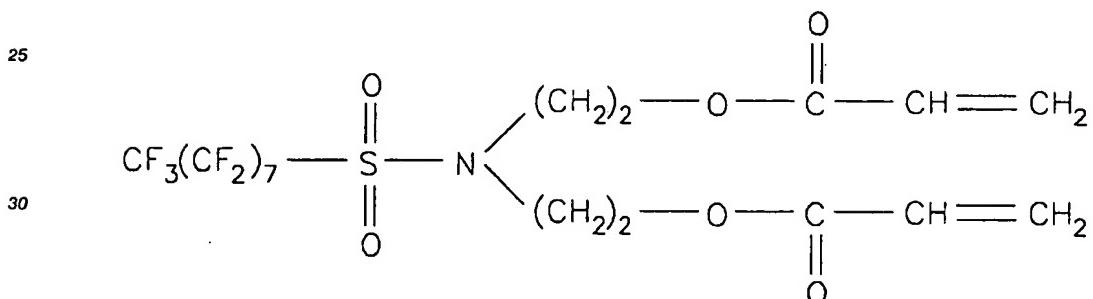
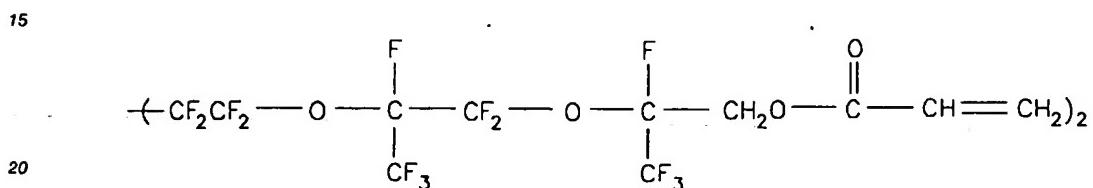
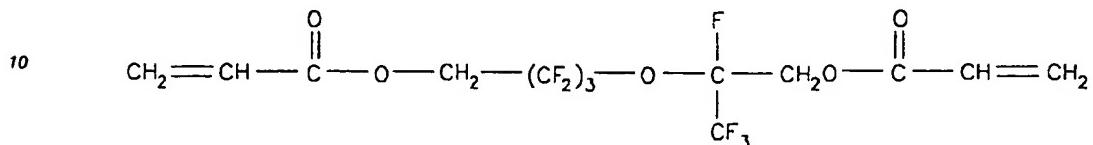
55



and



where X is a perfluoroalkylene grouping, or a perfluoroalkylene grouping in which one or more carbon atoms have been replaced by -O- linkages, and X' is a perfluoroalkyl group. Examples of such diacrylates are:



35 $\text{CH}_2=\text{CH}-\text{CO}-\text{OCH}_2-(\text{CF}_2)_n-\text{CH}_2\text{O}-\text{CO-CH=CH}_2$ ($n = 2, 3$ or 4)
 Diols suitable for preparing these diacrylates are available from Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, United States of America. A specific preferred diacrylate for use in the present process is that of the formula:

40 $\text{CH}_2=\text{CH}-\text{CO}-\text{OCH}_2\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n-\text{CF}_2-\text{CH}_2\text{O}-\text{CO-CH=CH}_2,$

(wherein m/n is in the range of 0.2:1 to 5:1), which is sold by Minnesota Mining and Manufacturing Company under the tradename L-9367.

45 The relative amounts of the copolymer and the fluorinated diacrylate in the photopolymerizable composition affect both the viscosity of the composition and the physical properties of the cladding produced. In general, it is desirable that the viscosity of the photopolymerizable composition be in the range of 1 Pas to 15 Pas (1000 to 15000 cP), since viscosities within this range are desirable to allow proper coating of optical fibers using conventional coating equipment. Photopolymerizable compositions comprising from 0.5 to 2 parts by weight of the copolymer per part by weight of the fluorosubstituted diacrylate monomer are preferred, since such compositions normally have a viscosity appropriate for coating and produce claddings with good physical properties.

50 The present invention can produce claddings with refractive indices less than about 1.35; indeed, as described in the Examples below, preferred processes of the present invention can produce claddings with refractive indices as low as 1.33.

55 Cladding of optical fibers by the process of the present invention may be effected using any of the conventional techniques known to those skilled in the art. In a preferred process, coating of an optical fiber with the photopolymerizable composition of the present invention is effected using the apparatus shown

schematically in the accompanying drawing. This apparatus, generally designated 10, comprises an oven 12 containing a glass preform. Beneath the oven 12 are disposed two coating cups 14 and 16, each containing the photopolymerizable composition. An ultraviolet lamp 18 (for example, a Fusion Research electrodeless ultraviolet mercury vapor lamp) is disposed below the coating cup 16, and a capstan 20 is disposed below the lamp 18. The apparatus further comprises a wind-up roll 22.

An optical fiber 24 is drawn from the oven 12 at a rate of approximately 0.5 m/sec. by the capstan 20, and passes through the coating cups 14 and 16. These cups are provided with downwardly-tapering conical bases, with the apex of each cone having a vertical bore passing therethrough, the diameter of this bore being equal to the desired diameter of the optical fiber coated with the photopolymerizable composition, so that the bore wipes excess photopolymerizable composition from the fiber. The fiber, with the uncured photopolymerizable composition thereon, is then traversed past the lamp 18, where the solution is cured to produce an adherent clear cladding on the optical fiber.

If desired, before being wound onto the roll 22, the clad fiber may be passed through additional coating cups and under an additional ultraviolet lamp to apply an over-cladding in order to protect the relatively soft cladding of the invention from blocking on the roll 22.

The compositions of the present invention may be used for cladding any optical fibers. They may, for example, be used for cladding the fibers of optical fiber lasers, such as those described in US-A-4 815 079. The fiber optic lasers described in this patent comprise a single-mode core disposed within a relatively large, multimode cladding such that the core is displaced from the center of the cross-section of the 20 cladding. The cladding is surrounded by a further layer (second cladding) to prevent radiation from propagating out of the cladding. The compositions of the present invention may be used to form the second cladding of such a optical fiber laser, and permit the refractive index of this cladding to be such as to produce a numerical aperture (given by:

$$25 \quad N.A. = (N_1^2 - N_2^2)^{\frac{1}{2}}$$

where N_1 is the refractive index of the first cladding and N_2 that of the second cladding) for the optical fiber greater than 0.4 in such an optical fiber laser.

From the foregoing, it will be seen that the processes of the present invention enable very low index 30 claddings to be produced on optical fibers without the development of haze or phase separation during the preparation of the photopolymerizable composition or the curing of that composition to form the cladding itself. Furthermore, application of the photopolymerizable compositions of the present invention to the optical fibers, and curing of the composition, can be achieved using conventional equipment.

The following Examples are now given, though by way of illustration only, to show details of preferred 35 reagents, conditions and techniques used in the present invention.

EXAMPLES

Example 1: Preparation of copolymer having pendant photoinitiating groups

40 This Example illustrates the preparation of a copolymer having pendant photoinitiating groups by reaction of a photoinitiator monomer having both a photoinitiating group and an acrylate group with a fluorosubstituted monoacrylate.

Darocur ZLI-3331 (6.0 g, formula and manufacturer given above) was purified by dissolving it in dichloromethane (10 mL), and the resultant solution was purified by flash chromatography on a silica gel (32-63 μ m) column with 3% diethyl ether in dichloromethane as the eluent, 50 mL fractions being collected. Fractions 15-45, which contained the pure product, were combined and the solvents removed on a rotary evaporator at room temperature. The resultant residue was dissolved in a dichloromethane/pentane mixture, and the solvents again removed on a rotary evaporator at room temperature; when most of the solvents had been removed, crystallization commenced, and a moderately high oil pump vacuum was applied to complete the crystallization. The resultant cream-colored solid was broken up, transferred to an amber glass jar to protect it from ultraviolet radiation, and dried to constant weight under vacuum at room temperature to yield 5.22 g. (87%) of a material melting at 55-56 °C.

L-9911 (360 g, formula and manufacturer given above) was purified by fractional distillation from a 250 mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, thermometer, 30 cm Vigreux column and a variable reflux ratio still head connected to a vacuum pump via a manometer and a liquid nitrogen cooled trap. Di-tert-butylhydroquinone was added to the flask as a polymerization inhibitor. The pressure was maintained at 5 mm Hg and the flask heated on an oil bath held at 95-121 °C. The fraction

distilling at 55-57°C at the column head was collected (158.5 g., 44%) and used in the preparation described below. This fraction was found to lack the infra-red peaks at 3500 cm⁻¹ (due to unreacted alcohol) and 1810 cm⁻¹ (due to trifluoroacetate impurities) present in the starting material.

- Purified Darocur ZLI-3331 (4.0 g) was dissolved in warm HFX (50 mL, previously purified by distillation through a Vigreux column) with swirling, and a small amount of insoluble polymer removed by filtration through cotton wool. The clear, filtered solution was added under argon to a 250 mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, thermometer and condenser. Purified L-9911 (96 g) was slowly poured into the flask with stirring, then additional HFX (50 mL) was added. Finally azobisis(isobutyronitrile) (100 mg) was added and the solution was stirred with the flask in an oil bath held at 60°C.
- Deoxygenation was effected by alternately evacuating the flask until HFX began to reflux, and then filling the flask with argon back to atmospheric pressure, this cycle being repeated five times.

After the reaction mixture had been stirred for 25 hours, the resultant viscous solution was transferred by pipette into acetone (600 mL, reagent grade) in a 1 L Erlenmeyer flask. The resultant acetone solution was decanted from the polymer gum, the gum washed with acetone, and the acetone again decanted. A fluorocarbon solvent (100 mL of Fluorinert FC-72, sold by Minnesota Mining and Manufacturing Company; this material is mainly C₆F₁₄ and has a boiling point of about 56°C) was added and the resultant white mixture transferred to a 250 mL, round-bottomed flask. Acetone and FC-72 were distilled from the flask under vacuum at room temperature using a rotary evaporator, and the two immiscible solvents recovered were separated. The Erlenmeyer flask was washed with the recovered FC-72, the washings were added to the polymer in the flask, and the resultant mixture was again distilled on the rotary evaporator, with the recycling of the FC-72 being repeated until no more acetone distilled and the polymer solution was clear. A final distillation of FC-72 from the polymer was effected at 25°C under 2 mm Hg pressure by attaching an oil pump to the rotary evaporator, and the polymer was then stored in vacuo at room temperature in the dark until a constant weight was obtained.

The copolymer thus prepared (87.3 g, 87% yield) was a clear, pale yellow, very viscous oil of refractive index (n_D^{25}) 1.3435. The copolymer (51.9 mg) was dissolved in 1,1,2-trichlorotrifluoroethane to a total volume of 10.0 mL and its inherent viscosity (η_{inh}) measured by a Cannon-Ubbelholde Dilution Viscometer size 50 found to be 0.08 dL/g. The copolymer was insoluble in trifluorotoluene (C₆H₅CF₃) and trifluoroethyl acetate (CH₃CO₂CH₂CF₃).

Example 2 : Preparation and curing of resin suitable for optical fiber cladding

This Example illustrates the preparation and curing of a resin suitable for use as an optical fiber cladding.

L-9367 (approximately 450 g) was purified by filtration through silica gel. Purified L-9367 thus prepared (87.3 g) was added to the copolymer (87.3 g) prepared in Example 1 above in a 250 mL round-bottomed flask. The resultant mixture was warmed on a steam bath, with manual rotation of the flask and magnetic stirring of the contents, to produce a clear, haze-free, pale yellow, viscous, homogeneous solution, which was transferred to a brown glass bottle while still warm. The net weight of the transferred solution was 171.7 g (98%), and its Brookfield viscosity was 3,850 Pa·s (3850 cP).

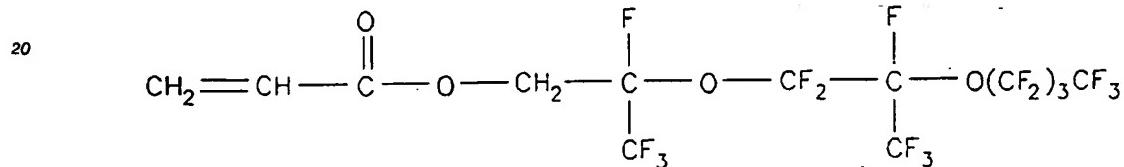
To demonstrate curing of this solution, a small quantity thereof was placed between two glass microscope slides (25 x 75 mm) separated by two thicknesses (approximately 0.25 mm) of Parafilm (sold by American Can Company, Greenwich CT 06830, United States of America). The refractive index (n_D^{23}), as measured by an Abbe refractometer with a drop of mineral oil between the refractometer prism and the slide sandwich, was 1.3270. The sandwich was then set 5 cm. below a water-cooled 450 W Hanovia medium pressure mercury lamp. After 10 seconds exposure $n_D^{23} = 1.3307$, after an additional 10 seconds exposure $n_D^{23} = 1.3312$, and after an additional 30 seconds exposure $n_D^{23} = 1.3315$.

The glass slides were then pried apart to reveal a very clear and flexible film which clung to glass well enough that its refractive index could be measured on the prism of the Abbe refractometer, $n_D^{22} = 1.3317$, $n_D^{25} = 1.3312$. Calculation of the refractive index from the dispersion reading of the Abbe refractometer gave $n_{807} = 1.3287$. Direct critical angle refractive index measurement of the cured polymer film sandwiched between two 45°, 45°, 90° glass prisms was effected on an optical bench with a goniometer and a titanium/sapphire laser tuned to 807 nm, giving $n_{807} = 1.3280$.

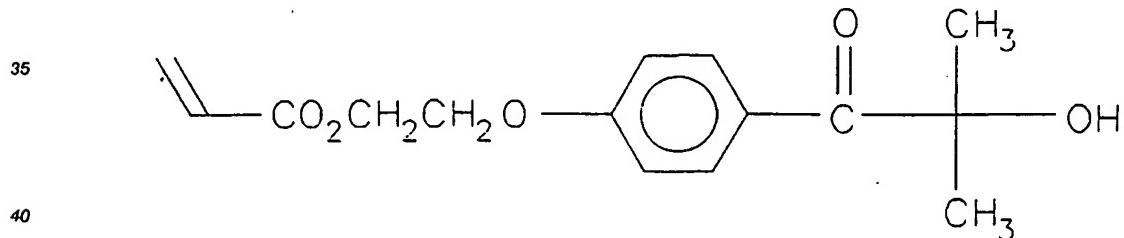
The photopolymerizable solution was also used to coat an optical fiber having a refractive index of about 1.45, and cured to produce a cladding on the fiber. The resultant cladding had a refractive index of about 1.33 and the clad fiber had a numerical aperture of about 0.59.

Claims

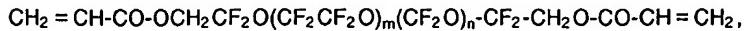
1. A process for cladding an optical fiber, which process comprises:
 5 coating the optical fiber with a layer of a photopolymerizable composition; and
 exposing the coated optical fiber to ultraviolet light, thereby curing the photopolymerizable
 composition to produce a cladding on the optical fiber,
 characterized in that the photopolymerizable composition comprises a fluorosubstituted diacrylate
 10 and a copolymer having repeating units from a fluorosubstituted monomer having an ethylenically
 unsaturated group, and repeating units from a photoinitiator monomer having both a photoinitiating
 group and an ethylenically unsaturated group, these repeating units from the photoinitiator monomer
 providing pendant photoinitiating groups in the copolymer.
2. A process according to claim 1 characterized in that the fluorosubstituted monomer comprises a
 15 monoacrylate or mono-methacrylate.
3. A process according to claim 2 characterized in that the fluorosubstituted monoacrylate comprises a
 fluorosubstituted polyether, preferably



4. A process according to any one of the preceding claims characterized in that the ethylenically
 30 unsaturated group of the photoinitiator monomer is an acrylate or methacrylate group, preferably an
 acrylate of a phenoxyalkanol or of a phenylalkanol.
5. A process according to claim 4 characterized in that the photoinitiator monomer comprises:



6. A photopolymerizable composition capable of being polymerized upon exposure to ultraviolet light and
 45 comprising a fluorosubstituted diacrylate, the composition being characterized in that it also comprises
 a copolymer as defined in any of the preceding claims.
7. A photopolymerizable composition according to claim 6 characterized by a viscosity in the range of
 50 1000 to 15000 cP.
8. A photopolymerizable composition according to claim 6 or 7 characterized in that the fluorosubstituted
 diacrylate monomer contains at least 25 percent by weight fluorine.
9. A photopolymerizable composition according to any one of claims 6 to 8 characterized in that the
 55 fluorosubstituted diacrylate monomer comprises

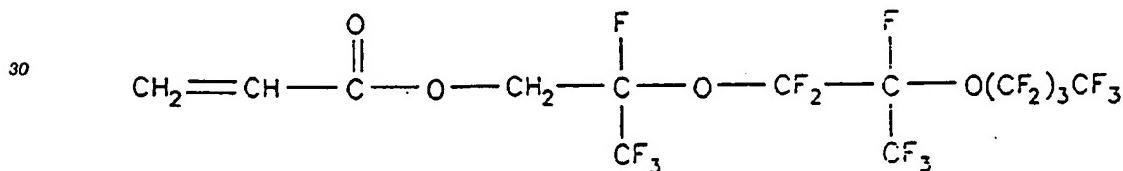


in which m/n is in the range of 0.2:1 to 5:1.

10. A photopolymerizable composition according to any one of claims 6 to 9 characterized in that it comprises from 0.5 to 2 parts by weight of the copolymer per part by weight of the fluorosubstituted diacrylate.

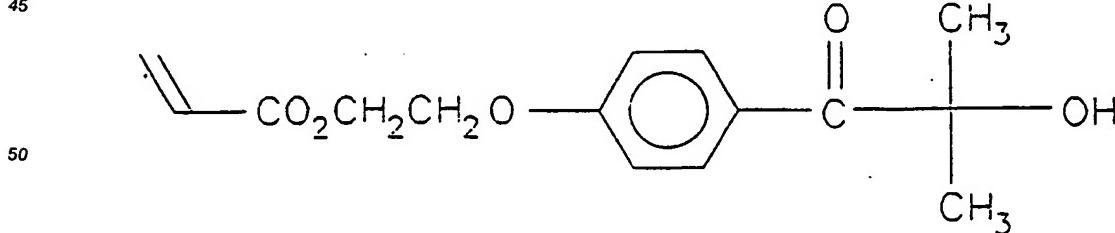
Patentansprüche

1. Verfahren zum Ummanteln einer optischen Faser, welches (folgende Schritte) umfaßt:
Beschichtung der optischen Faser mit einer Schicht einer photopolymerisierbaren Zusammensetzung; und
Belichten der beschichteten optischen Faser mit Ultravioletlicht, wobei die photopolymerisierbare Zusammensetzung unter Bildung einer Ummantelung auf der optischen Faser ausgehärtet wird,
dadurch gekennzeichnet, daß die photopolymerisierbare Zusammensetzung ein fluorsubstituiertes Diacrylat und ein Copolymer mit sich wiederholenden Einheiten eines fluorsubstituierten Monomers mit einer ethylenisch ungesättigten Gruppe und sich wiederholenden Einheiten aus einem Photoinitiator-Monomer mit einer photoinitiierenden Gruppe und einer ethylenisch ungesättigten Gruppe enthält,
wobei diese sich wiederholenden Einheiten aus dem Photoinitiator-Monomer abstehende photoinitiierende Gruppen im Copolymer bereitstellen.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das fluorsubstituierte Monomer ein Monoacrylat oder Mono-Methacrylat darstellt.
3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß das fluorsubstituierte Monoacrylat einen fluorsubstituierten Polyether, vorzugsweise



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darstellt.

4. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die ethylenisch ungesättigte Gruppe des Photoinitiator-Monomers eine Acrylat- oder Methacrylatgruppe, vorzugsweise ein Acrylat eines Phenoxyalkanols oder eines Phenylalkanols, darstellt.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß das Photoinitiator-Monomer enthält:

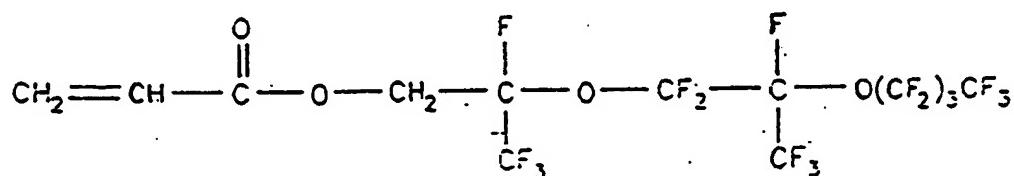


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6. Photopolymerisierbare Zusammensetzung, die bei Bestrahlung mit Ultravioletlicht polymerisierbar ist, und die ein fluorsubstituiertes Diacrylat enthält, wobei die Zusammensetzung dadurch gekennzeichnet ist, daß sie auch ein Copolymer, wie es in einem der vorhergehenden Ansprüche definiert ist, enthält.

7. Photopolymerisierbare Zusammensetzung nach Anspruch 6, gekennzeichnet durch eine Viskosität im Bereich von 1000 bis 15000 cP.
8. Photopolymerisierbare Zusammensetzung nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß das fluorsubstituierte Diacrylat-Monomer mindestens 25 Gew.-% Fluor enthält.
- 5 9. Photopolymerisierbare Zusammensetzung nach einem der Ansprüche 6 bis 8, dadurch gekennzeichnet, daß das fluorsubstituierte Diacrylat-Monomer
- 10 $\text{CH}_2 = \text{CH-CO-OCH}_2\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n-\text{CF}_2\text{CH}_2\text{O-CO-CH} = \text{CH}_2$,
- darstellt, worin m/n im Bereich von 0,2:1 bis 5:1 liegt.
- 15 10. Photopolymerisierbare Zusammensetzung nach einem der Ansprüche 6 bis 9, dadurch gekennzeichnet, daß sie 0,5 bis 2 Gew.-Teile Copolymer je Gewichtsteil fluorsubstituiertes Diacrylat enthält.

Revendications

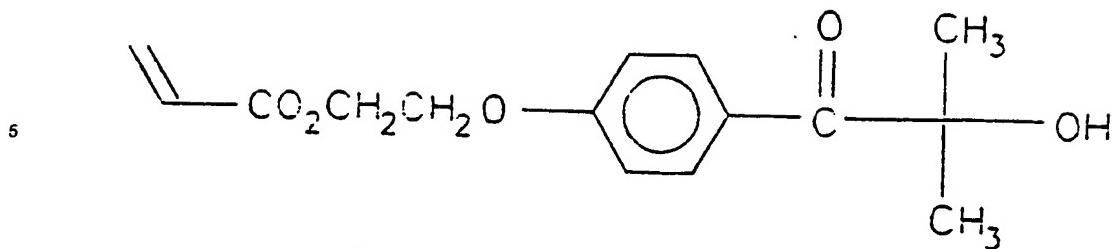
1. Procédé de gainage d'une fibre optique comprenant :
- 20 - l'enrobage de la fibre optique avec une couche d'une composition photopolymérisable et
- l'exposition de la fibre optique enrobée à de la lumière ultraviolette, durcissant ainsi la composition photopolymérisable afin de produire une gaine autour de la fibre optique,
caractérisé en ce que la composition photopolymérisable comprend un di acrylate fluoré et un
25 copolymère comportant des motifs répétitifs d'un monomère fluoré comportant un groupe à insaturation éthylénique et des motifs répétitifs d'un monomère photoamorceur comportant à la fois un groupe de photoamorçage et un groupe à insaturation éthylénique, les motifs répétitifs de monomère photoamorceur conférant au copolymère des groupes latéraux photoamorceurs.
2. Procédé conforme à la revendication 1, caractérisé en ce que le monomère fluoré englobe un
30 monoacrylate ou un monométhacrylate.
3. Procédé conforme à la revendication 2, caractérisé en ce que le monoacrylate fluoré englobe un polyéther fluoré, de préférence un composé de formule



4. Procédé conforme à une quelconque des revendications précédentes, caractérisé en ce que le groupe à insaturation éthylénique du monomère photoamorceur est un groupe acrylate ou méthacrylate, de préférence un groupe acrylate d'un phénoxyalcanol ou d'un phénylalcanol.
- 45 5. Procédé conforme à la revendication 4, caractérisé en ce que le monomère photoamorceur englobe un composé de formule

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6. Composition photopolymérisable capable d'être polymérisée par exposition à de la lumière ultraviolette et comprenant un diacrylate fluoré, la composition étant caractérisée en ce qu'elle contient également un copolymère défini dans une quelconque des revendications précédentes.
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7. Composition photopolymérisable conforme à la revendication 6, caractérisée par une viscosité comprise entre 1000 et 15 000 cP.
8. Composition photopolymérisable conforme à la revendication 6 ou 7 caractérisée en ce que le monomère de type diacrylate fluoré contient au moins 25 % en poids de fluor.
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9. Composition photopolymérisable conforme à une quelconque des revendications 6 à 8, caractérisée en ce que le monomère de type diacrylate fluoré comprend un composé de formule
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- $\text{CH}_2 = \text{CH-CO-OCH}_2\text{CF}_2\text{O}(\text{CF}_2\text{CF}_2\text{O})_m(\text{CF}_2\text{O})_n-\text{CF}_2-\text{CH}_2\text{O-CO-CH} = \text{CH}_2$,
- dans laquelle le rapport m/n est compris entre 0,2/1 et 5/1.
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10. Composition photopolymérisable conforme à une quelconque des revendications 6 à 9, caractérisée en ce qu'elle contient de 0,5 à 2 parties en poids du copolymère par partie en poids du diacrylate fluoré.

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